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## Scope of Research

We investigate the chemical phenomenon in two kinds of condensed phases. (1) To understand the chemical structure, property and reactions in a two-dimensional molecular aggregated ultrathin film, the keywords of molecular interactions and orientation are additionally employed, and the fluctuated molecular aggregates are investigated by originally developed spectroscopic and theoretical techniques. (2) The structure, dynamics, and reaction of solutions with nano-scale inhomogeneity and/or with fine tunability are investigated by computer simulation, and statistical-mechanical theory of solutions, and NMR spectroscopy.

### KEYWORDS

Infrared and Raman Spectroscopy	Free Energy
Surface and Interface Chemistry	Solvation
Spectral Analysis	Solution Theory



## Selected Publications

Kasuya, A.; Itoh, Y.; Okada, T.; Osawa, M.; Takahashi, Y.; Kazuma, E.; Tatsuma, T.; Hasegawa, T., Anisotropic Light Absorption by Localized Surface Plasmon Resonance in a Thin Film of Gold Nanoparticles Studied by Visible Multiple-Angle Incidence Resolution Spectrometry, *Phys. Chem. Chem. Phys.*, **13**, 9691-9696 (2011).

Muro, M.; Itoh, Y.; Hasegawa, T., A Conformation and Orientation Model of the Carboxylic Group of Fatty Acids Dependent on Chain Length in a Langmuir Monolayer Film Studied by Polarization-Modulation Infrared Reflection Absorption Spectroscopy, *J. Phys. Chem. B*, **114**, 11496-11501 (2010).

Sakabe, T.; Yamazaki, S.; Hasegawa, T., Analysis of Cross-Section Structure of a Polymer Wrapping Film Using Infrared Attenuated Total Reflection Imaging Technique with an Aid of Chemometrics, *J. Phys. Chem. B*, **114**, 6878-6885 (2010).

Karino, Y.; Matubayasi, N., Free-energy Analysis of Hydration Effect on Protein with Explicit Solvent: Equilibrium Fluctuation of Cytochrome *c*, *J. Chem. Phys.*, **134**, 041105-041108 (2011).

Sakuraba, S.; Matubayasi, N., Distribution-function Approach to Free Energy Computation, *J. Chem. Phys.*, **135**, 114108-114118 (2011).

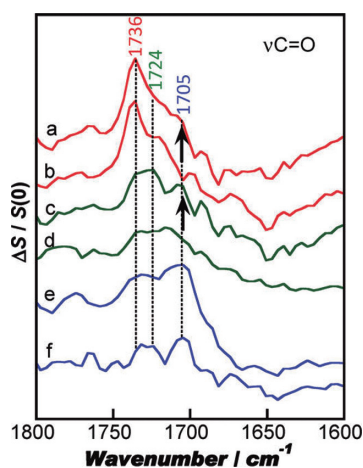
Takahashi, H.; Maruyama, K.; Karino, Y.; Morita, A.; Nakano, M.; Jungwirth, P.; Matubayasi, N., Energetic Origin of Proton Affinity to the Air/Water Interface, *J. Phys. Chem. B*, **115**, 4745-4751 (2011).

## Molecular Fine-Structure Analysis in a Monolayer at the Air/Water Interface

When a Langmuir-adsorbed monolayer film on water (L film) of a fatty acid is studied, L-film specific factors should be taken into account as well as the chain-length dependence; i.e. strong interactions with the water surface. In an L film of a fatty acid, the carboxylic group is considered to be in deep contact with the water surface, and hydration of the carboxylic group is therefore an inevitable factor to understand the character and structure of the L film.

To study the structures of both hydrocarbon chains and the carboxylic groups, infrared (IR) spectroscopy is powerful. To prevent the disturbance by water vapor, the technique of polarization-modulation infrared reflection absorption spectroscopy (PM-IRRAS) provides a convenient way to access the fingerprint region of IR spectra of L films.

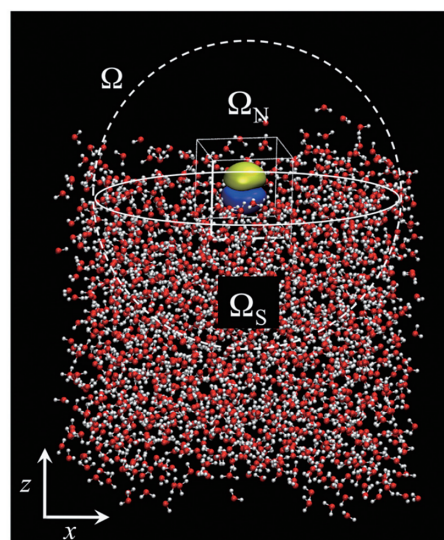
In our study, the conformation of the carboxylic group of fatty acids in a Langmuir (L) monolayer film on water was described in relation to the aggregation property of the hydrocarbon chain. Polarization-modulation infrared reflection absorption spectra (PM-IRRAS) of L films of heptadecanoic acid (C17), octadecanoic acid (C18) and nonadecanoic acid (C19) exhibited systematic spectral changes in both the C–H and C=O stretching vibration regions. Through a stabilization analysis of the L films at a high surface pressure, C19 L film has been found outstandingly stable exhibiting no film shrink, while the rest two compounds exhibit a large shrink at the high surface pressure. By taking into account the uniquely high aggregation property of the hydrocarbon chains of C19, the three major bands arising from the C=O stretching vibration mode propose three types of molecular conformations about the carboxylic group, which were elucidated by a balance of the hydration of the carboxylic group, the chain length of the hydrocarbon chain and the surface pressure.



**Figure 1.** PM-IRRAS spectra of Langmuir monolayers of fatty acids with three different chain lengths (C17~C19) as a function of surface pressure in the C=O stretching vibration region.

## Energetic Origin of Proton Affinity to the Air/Water Interface

The affinity of the hydronium ion to the air/water interface is an issue recently studied intensively by both experimental and theoretical approaches. To investigate the mechanism responsible for the surface propensity of this ion, we performed a series of novel quantum-mechanical/molecular-mechanical simulations combined with the energy-representation theory of solutions. The solvation free energy of the  $\text{H}_3\text{O}^+$  solute placed at the interface was obtained as -98 kcal/mol, being more stable by 4 kcal/mol than in the bulk. We further decomposed the solvation free energies into contributions from the water molecules residing in the oxygen and the hydrogen sides of the solute, as shown in Figure 2, to clarify the origin of the surface preference. When the solute was displaced from the bulk to the interface, it was shown that the free energy contribution from the oxygen side is destabilized by ~10 kcal/mol because of a reduction of the number of surrounding solvent water molecules. It was observed, however, that the free energy contribution from the hydrogen side is unexpectedly stabilizing and surpasses the destabilization in the opposite side. We found that the stabilization in the hydrogen side originates from the solute-solvent interaction in the medium range beyond the nearest neighbor. It was also revealed that the solute's electronic polarization amounts to half the stabilization free energy change associated with the solute displacement from the bulk to the interface.



**Figure 2.** A QM/MM snapshot for the hydronium ion placed at  $z = -2.0$  Å. The north and south hemispheres,  $\Omega_N$  and  $\Omega_S$ , are also presented. The cubic box in the Figure indicates the real-space grid cell to enclose the wave function of the QM solute. The yellow and the blue surfaces represent the positive and negative isosurfaces for the HOMO of the solute with the values of  $\pm 0.001$  a.u., respectively.